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(54) **Method of preparing amino-, imino- and nitrilocarboxylic acids and silver-promoted copper catalyst for use in said method**

(57) A method is described for preparing amino-, imino-, and nitrilocarboxylic acids of formula



and alkaline salts of these, here R₁, R₂, and R₃, which may be the same or different, represent: hydrogen, n alkyl group having 1-10 C atoms, carboxyalkyl group having 1-10 C atoms [in the alkyl moiety], n aminoalkyl group having 1-10 C atoms [in the alkyl moiety], carboxycycloalkyl group having 3-6 C atoms [in the cycloalkyl moiety], a cycloalkyl-alkyl group having 3-6 C atoms in the cycloalkyl moiety and 1-10 C atoms in the alkyl moiety and having a carboxy group substituent, or an alkylcycloalkyl group having 1-10 C atoms in the alkyl moiety and 3-6 C atoms in the cycloalkyl moiety and having a carboxy group substituent; wherewith said alkyl groups may be linear or branched; and wherewith at least one of the groups R does not represent hydrogen; the method comprising:

(a) subjecting alkanolamines of formula



wherein the groups R' have the same significations as set forth above for the groups R, except that the aforesaid carboxy groups are hydroxyl groups, to an oxidative dehydrogenation reaction in aqueous alkaline medium in the presence of a copper catalyst of the Raney type promoted with 50-5000 ppm silver;

(b) separating the resulting carboxylate salts from

the reaction medium, and (optionally) purifying said salts or converting them to the corresponding amino acids by precipitation in acid medium;

(c) separating the catalyst from the reaction medium, washing said catalyst with demineralized water, and (optionally) recycling the catalyst to re-use in step (a) [(of the same or another production run)]; and

(d) recovering and collecting the hydrogen liberated in the reaction.

Also described is a catalyst for use in the described method. The catalyst is comprised of a Raney-type catalyst comprised of copper promoted with 50-5000 ppm silver supplied as follows:

- incorporated in an alloy;
- deposited on [the] surface from salts of silver; or
- in a physical mixture comprising finely divided metallic silver.

The compounds of formula (I) have been found to be important synthesis intermediaries, e.g. in preparation of N-phosphonomethylglycine (the herbicidal agent known as glyphosate).

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Description

[0001] A method is described for preparing amino-, imino-, and nitrilcarboxylic acids, and their alkaline metal salts, starting with alkanolamines. The method employs oxidative dehydrogenation of the alkanolamine(s) in an alkaline hydroxide medium, using as a catalyst a silver-promoted activated copper.

[0002] Also described is a silver-promoted activated copper catalyst for used in said method.

[0003] The subject amino-, imino-, and nitrilcarboxylic acids have the following formula:



where R_1 , R_2 , and R_3 , which may be the same or different, represent:

hydrogen,
 an alkyl group having 1-10 C atoms,
 a carboxyalkyl group having 1-10 C atoms [in the alkyl moiety], an aminoalkyl group having 1-10 C atoms [in the alkyl moiety],
 a carboxycycloalkyl group having 3-6 C atoms [in the cycloalkyl moiety],
 a cycloalkyl-alkyl group having 3-6 C atoms in the cycloalkyl moiety and 1-10 C atoms in the alkyl moiety and having a carboxy group substituent, or
 an alkyl-cycloalkyl group having 1-10 C atoms in the alkyl moiety and 3-6 C atoms in the cycloalkyl moiety and having a carboxy group substituent;

wherewith said alkyl groups may be linear or branched;
 and wherewith at least one of the groups R does not represent hydrogen.

[0004] The described method comprises the following:

(a) Subjecting alkanolamines of formula



wherein the groups R' have the same significations as set forth above for the groups R, except that the aforesaid carboxy groups are hydroxyl groups, to an oxidative dehydrogenation reaction in aqueous alkaline medium in the presence of a copper catalyst of the Raney type promoted with 50-5000 ppm silver;

(b) Separating the resulting carboxylate salts from the reaction medium, and (optionally) purifying said salts or converting them to the corresponding amino acids by precipitation in acid medium;

(c) Separating the catalyst from the reaction medium, washing said catalyst with demineralized water, and (optionally) recycling the catalyst to re-use in step (a) [(of the same or another production run)]; and

(d) Recovering and collecting the hydrogen liberated in the reaction.

[0005] The compounds of formula (I) have been found to be important synthesis intermediaries, e.g. in preparation of N-phosphonomethylglycine (the herbicidal agent known as glyphosate).

[0006] The activated copper, promoted with silver [e.g.] via silver salts, has the advantage that reactivation with each re-use [of the catalyst] is not required. If an un-promoted activated copper is used, or if an activated copper promoted with a metal (or metals) other than silver (e.g. chromium, nickel, molybdenum, tungsten, vanadium, titanium, niobium, manganese, zirconium, cobalt, or mixtures of these) is used, the catalyst activity fades rapidly with successive reactions.

[0007] For the better part of 200 years, it has been known to convert alcohols to alkaline metal salts of the corresponding carboxylic acids by heating the alcohols with alkaline metal hydroxides (Dumas, 1840, 35 Ann. 129-73).

[0008] The reaction has been extended to aminoalcohols; when these are heated in the presence of an alkaline metal compound they undergo oxidative dehydrogenation to yield the alkaline metal salt of the corresponding amino- or iminoacid; this occurs even without a catalyst (U.S. Pat. 2,384,816), preparation of glycine in low yield from diethanolamine and KOH). Known catalysts for use with this reaction include, e.g., cadmium oxide, zinc oxide, palladium, platinum, and activated copper. Hydrogen is liberated. Oxygen or a gas containing oxygen may be introduced to form water from the hydrogen and thereby avoid hazardous accumulations of hydrogen.

[0009] Examples from the patent literature:

-- U.S. 2,384,817 (1945), preparation of glycine from monoethanolamine (MEA) and potassium hydroxide at ele-

vated temperature, in an anhydrous medium, with an activated copper catalyst (low yield);

-- U.S. 3,842,081 (1974), preparation of iminodiacetic acid (IDA) from diethanolamine (DEA) and potassium hydroxide, with a cadmium oxide catalyst (good yield, but cadmium is deemed a toxic substance);

-- U.S. 3,578,709 (1971), preparation of nitrilotriacetic acid (NTA) from triethanolamine (TEA) and an alkaline metal hydroxide, with a zinc oxide catalyst (low yield);

-- Jap. Pat. 53/7709, preparation of IDA and NTA from DEA and TEA, [respectively,] in a sodium oxide medium, with a catalyst comprised of Pd or Pt supported on carbon, with injection of oxygen or a gas containing oxygen (low yields, in the order of 70%, and costly precious metal catalysts used to produce a product of relatively low net value);

-- U.S. Pat. 4,782,183, preparation of glycine, IDA, and NTA, from MEA, DEA, and TEA, respectively, and a hydroxide of an alkaline metal in aqueous medium, with an activated copper catalyst, at pressures up to 980 kPa (conversion very good) (as in the preceding examples, hydrogen liberated in the amount of 2 hydrogen atoms per acetic group, and the further disadvantage pertains that the copper cannot be re-used but must be replaced by fresh copper for each synthesis run, because it becomes depleted (poisoned) in a single use);

-- U.S. 5,367,112 (1994), preparation of glycine, IDA, and NTA, from MEA, DEA, and TEA, respectively, under the same conditions as in the above-cited patent, but wherewith the activated copper catalyst is promoted with 50-10,000 ppm of an element selected from the group comprising chromium, titanium, niobium, tantalum, tungsten, zirconium, vanadium, molybdenum, manganese, cobalt, nickel, or a mixture of these, the concentration of the catalyst being very high, viz, double that used according to U.S. Pat. 4,782,183;

-- U.S. Pat. 5,225,592 (1993), preparation of glycine, IDA, and NTA, from the corresponding alkanolamines and sodium hydroxide, with an activated copper [catalyst], all in aqueous medium and with injection of oxygen or an oxygen-containing gas to avoid emission of hydrogen, the avoidance being achieved viz. by formation of water with the oxygen. Pressure of the system maintained at values up to 11,765 kPa. Drawback again that a new catalyst must be used for each synthesis run;

-- [PTO Pat. App.] WO 92/06069, regeneration of activated copper used as a catalyst in synthesis of acetic acid derivatives, e.g. preparation of glycine, IDA, and NTA via oxidative dehydrogenation of MEA, DEA, and TEA, respectively. The regeneration is needed because the catalyst loses substantial activity, wherewith in practice [(absent regeneration)] it cannot be used more than once and therefore is not economical for industrial applications. In the regeneration, after each synthesis run the copper is treated in an aqueous solution of formaldehyde. A drawback is that effluents resulting from formaldehyde solutions are bactericidal, which creates a disposal problem.

[0010] As mentioned above, the above-described Raney copper catalysts, possibly promoted with chromium, molybdenum, titanium, niobium, tantalum, vanadium, zirconium, manganese, tungsten, cobalt, nickel, or with mixtures of these, all experience an appreciable loss of activity with successive uses after the first synthesis run, necessitating re-activation. The loss of activity is attributable to formation of cuprous and cupric oxides on the surface of the copper particles.

[0011] Surprisingly, it was discovered, in connection with the present invention, that the herein described incorporation of silver in the activated copper will greatly increase the catalyst yield as well as substantially increasing the number of synthesis runs for which the catalyst can be used (and re-used). Moreover, savings in catalyst used of up to 50% can be achieved in comparison to the amounts needed according to the above-described prior art patents. The effect is believed to be due to electrochemical protection of the copper by the silver, which reduces or prevents oxidation of the copper, according to the principle whereby the ratio of the areas of the cathode (Cu) and anode (Ag) is a factor in determining whether or not the less noble metal [(Cu)] corrodes.

[0012] The basis for this is that for a given current in an electrochemical cell the current density at an electrode depends on the area of the electrode, wherewith the current density is larger for a smaller electrode and vice versa. Accordingly, when one has an anode [sic -- evidently should be cathode] comprised of a less noble metal (Cu) with a surface area much greater than that of the cathode [sic -- evidently should be anode] comprised of a more noble metal (Ag), the current density at the anode will be much less than that at the cathode, and therefore the corrosion suffered by the anode will be minimal. This protective effect, which can be observed by the naked eye as a simple color change if the catalyst is used without a promoter, in comparison to no color change in the promoted catalyst, was clearly established by examination in an electron microscope at magnifications of 150 X and 5000 X. Particles of un-promoted activated copper, and particles of silver-promoted activated copper as described in the present patent application, were subjected to such an examination before and after use, which examination revealed significant differences in the appearance of the un-promoted compared to the promoted activated copper, which stemmed from structural differences in the particles. The micrographs of the un-promoted Raney copper taken before and after use [of the catalyst] appeared very different -- the unused particles had a surface which, while irregular, had a uniform and continuous surface appearance, whereas the used particles showed areas of reduced thickness, with deep fissures and meandering depressions. In contrast, the silver-promoted copper particles had nearly the identical appearance before and after use,

indicating a chemical and electrochemical protective effect of the silver on the copper. Consequently, the silver-promoted Raney copper catalyst had a longer service life than the un-promoted Raney copper catalyst.

[0013] The aminoalcohols which may be used in the context of the claimed method are: MEA, DEA, TEA, N-methylethanolamine, N-ethylethanolamine, N-isopropylethanolamine, N-butylethanolamine, N-nonylethanolamine, N-(2-aminoethyl)ethanolamine, N-(3-aminopropyl)ethanolamine, N,N-dimethylethanolamine, N,N-diethylethanolamine, N,N-dibutylethanolamine, N-methyl-N,N-diethanolamine, N-ethyl-N,N-diethanolamine, N-isopropyl-N,N-diethanolamine, N-butyl-N,N-diethanolamine, N-ethyl-N-(2-aminoethyl)ethanolamine, and N-methyl-N-(3-aminopropyl)ethanolamine.

[0014] The initial concentration of the alkanolamines may be in the range 15-35 wt.% (based on the total initial weight of the reaction components), preferably 26-30 wt.%. For concentrations above 30 wt.%, solubility problems may be encountered, and for concentrations below 26 wt.%, correspondingly lower productivity is experienced.

[0015] The silver-promoted Raney copper catalyst is comprised of copper activated by treating an Al-2Cu alloy with sodium hydroxide, by methods which are per se known. The silver promoter is incorporated in the alloy; or is applied by precipitation on the activated copper by treatment in alkaline medium, from silver salts such as the nitrate, fluoride, chlorate, perchlorate, or lactate, or is provided via simple mixture of activated copper with 50-5000 ppm of finely divided metallic silver.

[0016] The amount of catalyst added is in the range 5-25 [wt.]% (based on the [weight of the] alkanolamine to be reacted), preferably 8-12 [wt.]. At these concentrations, better results are obtained than with un-promoted Raney copper catalyst, or with a Raney copper catalyst promoted with chromium, vanadium, titanium, molybdenum, tungsten, manganese, cobalt, nickel, or mixtures of these [(sic -- omits niobium, tantalum, and zirconium)].

[0017] The solvent is water, to which an alkaline hydroxide has been added in a molar ratio with respect to the alkanolamine which is in the range (stoichiometric) to (stoichiometric + 15%); preferably the alkaline hydroxide is added in a stoichiometric amount or in a 5% molar excess. The hydroxide may be that of any alkaline metal (e.g. lithium, sodium, or potassium), provided that the salts of said hydroxide with the synthesized amino acid are soluble in the reaction medium at the synthesis temperature [and pressure].

[0018] The reaction is carried out at 100-220°C, preferably 120-190°C, at a pressure in the range 490-1470 kPa, preferably 784-1170 kPa, particularly preferably 883-980 kPa.

[0019] The conversion of the alkanolamine to the corresponding amino acid occurs with liberation of hydrogen. The hydrogen may be compressed and stored for use in other processes.

[0020] The invention will be illustrated by way of the following Examples.

Example 1 [(comparison example)]:

[0021] In this Example, the results obtained are those from a method of preparing an amino acid from an alkanolamine, wherewith the catalyst used is an activated copper catalyst which is not promoted (doped) with another metal.

[0022] Into a 3.5 l pressure reactor comprised of type "316" stainless steel and having an agitator, there were charged:

- 1070 g (10 mol) 99% diethanolamine (DEA);
- 1739 g (20 mol) 46 wt.% [aqueous] NaOH;
- 2033 g demineralized water; and
- 115.5 g (dry basis) activated copper (Raney-type product) (comprising 210 g of 55 wt.% copper prepate in water).

[0023] With the reactor hermetically sealed, the mixture was heated to a point of temperature 120°C, pressure 980 kPa, at which time purging of the H₂ produced [sic -- evidently purging with nitrogen] was begun, in a manner such that the temperature [rose] to 160-180°C, with the pressure being maintained at 882-980 kPa. The reaction was continued under these conditions [of temperature and pressure, with agitation], until no further hydrogen appeared to be emitted [(based on monitoring)], which took 4 hr. Continuing the agitation, the resulting solution of sodium iminodiacetate with suspended activated copper was cooled to 70°C. The solution of [sodium] iminodiacetate [was separated out and] was sent to precipitation of iminodiacetic acid.

[0024] The activated copper was washed with demineralized water, fresh copper [catalyst] in the amount of 2.5 [wt.]% was added (dry basis) [(sic -- evidently 0.025 x the 115.5 g originally employed)] to compensate for the losses in handling, and the activated copper [catalyst prepate] was then re-used in a new synthesis.

[0025] [The procedure was repeated, thereby testing the catalyst in 1 initial and 2 re-uses.]

[0026] The results are set forth in Table 1.

Table 1

Conversion of DEA to IDA (iminodiacetic acid), in a number of synthesis runs, using (and re-using) as catalyst the same activated copper catalyst:		
Synthesis run	Conversion to IDA (%)	Reaction time (hr)
1	99.8	4.0
2	88.7	4.5 ¹
3	68.2	5.0 ¹

Footnote 1: After this period of time, the reaction rate had slowed to essentially zero, with no more hydrogen being liberated, wherewith the intermediate formed [which was present at that time] was not catalyzed to be finally converted to IDA.

Example 2:

[0027] The process was carried out with the same equipment, the same concentrations of raw materials, and the same conditions of pressure and temperature as in Example 1, but the activated copper employed was promoted with 1000 ppm chromium, which was incorporated in an alloy, Al-2Cu. The results of the experiments are presented in Table 2.

Table 2

Conversion of DEA to IDA (iminodiacetic acid), in a number of synthesis runs, using (and re-using) as catalyst the same activated copper catalyst (promoted with 1000 ppm chromium incorporated in an alloy [Al-2Cu]):		
Synthesis run	Conversion to IDA (%)	Reaction time (hr)
1	99.5	4.5
2	70	5.0 ¹

Footnote 1: After this period of time, the reaction rate had slowed to essentially zero, with no more hydrogen being liberated, wherewith the intermediate formed [which was present at that time] was not catalyzed to be finally converted to IDA.

Example 3:

[0028] The process was carried out with the same equipment, the same concentrations of raw materials, and the same conditions of pressure and temperature as in Example 1, but the activated copper employed in each synthesis [run] was promoted with 100 ppm chromium, which was added in the form of a [sic] salt. The results of the experiments are presented in Table 3.

Table 3

Conversion of DEA to IDA (iminodiacetic acid), in a number of synthesis runs, using (and re-using) as catalyst in each synthesis [run] the same activated copper catalyst (promoted with 100 ppm chromium in the form of a [sic] salt):		
Synthesis run	Conversion to IDA (%)	Reaction time (hr)
1	99.9	4.5
2	91.8	5.0 ¹
3	84	5.7 ¹
4	68	6 ¹

Footnote 1: After the stated period of time, the reaction rate had slowed to essentially zero, with no more hydrogen being liberated, wherewith the intermediate formed [which was present at that time] was not catalyzed to be finally converted to IDA.

Example 4:

[0029] The process was carried out with the same equipment, the same concentrations of raw materials, and the same conditions of pressure and temperature as in Example 1, but the activated copper employed was promoted with 1000 ppm silver, which was added in the form of silver nitrate in the first synthesis run.

[0030] The results of the experiments are presented in Table 4.

Table 4

Conversion of DEA to IDA (iminodiacetic acid), in a number of synthesis runs, using (and re-using) as catalyst the same activated copper catalyst (promoted with 1000 ppm silver added in the form of silver nitrate in the first synthesis run):		
Synthesis run	Conversion to IDA (%)	Reaction time (hr)
1	96.8	4.5
2	92.0	5 ¹
3	89.6	5.5 ¹
4	90.3	5.5 ¹
5	88.9	5.3 ¹
8	90.0	5.6 ¹
10	89.1	5.5 ¹

Footnote 1: After this period of time, the reaction rate had slowed to essentially zero, with no more hydrogen being liberated, wherewith the intermediate formed [which was present at that time] was not catalyzed to be finally converted to IDA.

Example 5:

[0031] The process was carried out with the same equipment, the same concentrations of raw materials, and the same conditions of pressure and temperature as in Example 1, but the activated copper employed was promoted with 1000 ppm silver, which was added in the form of silver fluoride in the first synthesis run.

[0032] The results are presented in Table 5.

Table 5

Conversion of DEA to IDA (iminodiacetic acid), in number of synthesis runs, using (and re-using) as catalyst the same activated copper catalyst (promoted with 1000 ppm silver added in the form of silver fluoride in the first synthesis run):		
Synthesis run	Conversion to IDA (%)	Reaction time (hr)
1	93.5	4.0
2	91.7	4.6 ¹
3	88.6	5.0 ¹
4	90.4	4.8 ¹
5	88.4	5.1 ¹
8	90.3	5.3 ¹
10	89.3	5.1 ¹

Footnote 1: After this period of time, the reaction rate had slowed to essentially zero, with no more hydrogen being liberated, wherewith the intermediate formed [which was present at that time] was not catalyzed to be finally converted to IDA.

Example 6:

[0033] Into a 15 L pressure reactor comprised of type "316" stainless steel and having an agitator, there were charged:

- 2921 g (27.3 mol) 99% diethanolamine (DEA);
- 4747.5 g (54.6 mol) 46 wt.% [aqueous] NaOH;
- 5550 g demineralized water; and
- 315.3 g (dry basis) activated copper (Raney-type product), promoted with 1000 ppm silver added during the formation of an aluminum alloy, Al-2Cu.

[0034] With the reactor hermetically sealed, the mixture was heated to a point of temperature 120°C, pressure 980 kPa, at which time purging of the H₂ produced [sic -- evidently purging with nitrogen] was begun, in a manner such that the temperature [rose] to 160-180°C, with the pressure being maintained at 882-980 kPa. The reaction was continued under these conditions [of temperature and pressure, with agitation], until no further hydrogen appeared to be emitted [(based on monitoring)]. This practical end point was reached in 4.2 hr in the first synthesis run; the tenth synthesis run took 25% more time. Continuing the agitation, the resulting solution of sodium iminodiacetate with suspended activated copper was then cooled to 70°C. The solution of [sodium] iminodiacetate [was separated out and] was sent to precipitation of iminodiacetic acid.

[0035] The activated copper was washed with demineralized water, fresh copper [catalyst] in the amount of 2.5 [wt.]% was added (dry basis) [(sic -- evidently 0.025 x the 315.3 g originally employed)] to compensate for the losses in handling, and the activated copper [catalyst mixture] was then re-used in a new synthesis.

[0036] [The procedure was repeated, thereby testing the catalyst in 1 initial and 9 re-uses.]

[0037] The results are set forth in Table 6.

Table 6

Conversion of DEA to IDA (iminodiacetic acid), in a number of synthesis runs, using (and re-using) as catalyst the same activated copper catalyst (promoted with 1000 ppm silver added during the formation of an aluminum alloy, Al-2Cu):		
Synthesis run	Conversion to IDA (%)	Reaction time (hr)
1	96.0	4.2
2	93.4	4.5
3	90.5	4.9 ¹
4	90.6	4.8 ¹
5	89.7	5.0 ¹
8	87.5	4.9 ¹
10	90.1	5.4 ¹

Footnote 1: After this period of time, the reaction rate had slowed to essentially zero, with no more hydrogen being liberated, wherewith the intermediate formed [which was present at that time] was not catalyzed to be finally converted to IDA.

Example 7:

[0038] The process was carried out with the same equipment, the same concentrations of raw materials, and the same conditions of pressure and temperature [with agitation,] as in Example 6, but the activated copper employed was promoted with 1000 ppm silver, which was added in granular form in the first synthesis run.

[0039] The results are presented in Table 7.

Table 7

Conversion of DEA to IDA (iminodiacetic acid), in a number of synthesis runs, using (and re-using) as catalyst the same activated copper catalyst (promoted with 1000 ppm silver added in granular form):		
Synthesis run	Conversion to IDA (%)	Reaction time (hr)
1	95.5	4.5
2	93.1	5.0
3	90.1	5.5 ¹
4	90.0	5.6 ¹
5	88.5	5.6 ¹
8	87.0	5.5 ¹
10	89.8	5.8 ¹

Footnote 1: After this period of time, the reaction rate had slowed to essentially zero, with no more hydrogen being liberated, wherewith the intermediate formed [which was present at that time] was not catalyzed to be finally converted to IDA.

Claims

1. A method of preparing amino-, imino-, and nitrilocarboxylic acids of formula



(I)

5 hydrogen,
an alkyl group having 1-10 C atoms,
a carboxyalkyl group having 1-10 C atoms [in the alkyl moiety],
an aminoalkyl group having 1-10 C atoms [in the alkyl moiety],
a carboxycycloalkyl group having 3-6 C atoms [in the cycloalkyl moiety],
10 a cycloalkyl-alkyl group having 3-6 C atoms in the cycloalkyl moiety and
1-10 C atoms in the alkyl moiety and having a carboxy group substituent, or
an alkyl-cycloalkyl group having 1-10 C atoms in the alkyl moiety and 3-6 C atoms in the cycloalkyl moiety
and having a carboxy group substituent;

(a) subjecting alkanolamines of formula

wherein the groups R' have the same significations as set forth above for the groups R, except that the aforesaid carboxy groups are hydroxyl groups,

25 to an oxidative hydrogenation reaction in aqueous alkaline medium in the presence of a copper catalyst of the Raney type promoted with 50-5000 ppm silver;

(b) separating the resulting carboxylate salts from the reaction medium, and (optionally) purifying said salts or converting them to the corresponding amino acids by precipitation in acid medium;

(c) separating the catalyst from the reaction medium, washing said catalyst with demineralized water, and

30 (optionally) recycling the catalyst to re-use in step (a) [(of the same or another production run)]; and

(d) recovering and collecting the hydrogen liberated in the reaction.

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European Patent
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EUROPEAN SEARCH REPORT

Application Number
EP 00 11 3545

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The present search report has been drawn up for all claims			
Place of search BERLIN		Date of completion of the search 5 October 2000	Examiner Rufet, J
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EPO FORM 1503 (2.8.92) (P06001)

**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

EP 00 11 3545

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.
The members are as contained in the European Patent Office EDP file on
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